



Pyrolysis behaviors of two coal-related model compounds on a fixed-bed reactor

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ABSTRACT

The bibenzyl (BB) and benzyloxybenzene (BOB) were selected as coal-related model compounds, and their pyrolysis behaviors between 500 °C and 700 °C were investigated on a fixed-bed reactor. The pyrolysis products were analyzed by gas chromatography–mass spectrometer (GC–MS) and gas chromatography (GC), and the bond dissociation energy (BDE) was calculated with density functional theory (DFT) methods at B3LYP/6-31G (d) level. The results showed that the conversion in pyrolysis of BOB was higher than that of BB. The pyrolysis product distributions and BDE calculation indicate that C_{aliphatic}–C_{aliphatic} bond dissociation is the primary step for BB pyrolysis, while C_{aliphatic}–O bond dissociation is the primary step for BOB pyrolysis. The differences in pyrolysis behaviors between BB and BOB indicate that the existence of oxygen atom will reduce the BDE thus being preferentially dissociated under pyrolysis. The initial radicals should be stabilized by some more reactive radicals, which lead to higher liquid yield.

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1. Introduction

Coal is the main energy resource in China, and low rank coal deposits are accounting for more than 40% of the total coal reserves. About 90% of the low rank coal was consumed by power generation with direct combustion in past decades, which seriously pollutes the environment with low efficiency in energy utilization [1,2].

In order to improve the coal thermochemical conversion process, the fundamental study of coal structure and reaction mechanism during coal conversion is necessary. However, many single reactions take place simultaneously during the pyrolysis process, and the experimental results represent the total effects of all these reactions [3]. Furthermore, since different coal exhibits different coalification degree, reactivity and structure of coal should be varied [4]. As a result, it is very difficult to describe coal pyrolysis clearly. Although the structure of coal is complex, the types of weak covalent bond in coal are relatively simple. The clear understanding of the pyrolysis behavior of the typical bonds in coal will be beneficial for us to understand the pyrolysis process of the real coal.

The model compounds, which contain the main structure and property of the aromatic heterocyclic ring and simplify the macromolecule, have been widely used to study the structure and reactivity of coal. Bibenzyl (BB) has been commonly chosen as the model compound to represent the typical C_{aliphatic}–C_{aliphatic} weak bond in coal. Thermolysis of BB in gas and liquid phases has been extensively investigated [5–8].

and the results have been reviewed by Marvin L. Poutsma [9]. It is generally accepted that the homolytic cleavage of C_{aliphatic}–C_{aliphatic} bond to form benzyl radicals is the primary process, and toluene was the primary product when there was no catalyst, while stilbene was the primary product when CaO was used as catalyst [8]. When BB was immobilized on a silica surface, the pyrolysis pathway was influenced by diffusional constraints. As a result, surface-attached 1,1-diphenylethane which originated from the rearrangement reaction was the primary product [10]. The existence of oxygen in low rank coal can seriously influence the pyrolysis behavior. The pyrolysis of benzyloxybenzene (BOB), which has the typical C_{aliphatic}–O weak bond, has been extensively investigated as a model for labile ether bridges [11–20]. BOB pyrolysis is initiated by homolytic scission of the weak C_{aliphatic}–O bond to produce benzyl and phenoxy radicals. Toluene and phenol are the dominant products. However, recombination of the incipient radicals through coupling at phenoxy ring carbons to form benzylphenol isomers was also an important pathway during the BOB pyrolysis process [18]. In order to understand the experimental results thoroughly, quantum chemistry calculation was also widely applied in the pyrolysis mechanism study of model compounds [21–26].

The studies of BB and BOB pyrolysis behavior were abundant, but very few researches were conducted on a fixed-bed reactor. However, most of the coal pyrolysis experiments are conducted on fixed-bed reactors. In order to understand the connection of pyrolysis mechanism between real coal and coal-related model compounds, the pyrolysis experiments of BB and BOB were conducted on a fixed-bed reactor with a stainless steel tube in this study. Pyrolysis pathways were proposed based on related experimental results

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and previous studies. In addition, the bond dissociation energies (BDEs) for main radical pathways were calculated with Gaussian 09 suite of programs. The quantitative analysis of the pyrolysis products combined with quantum mechanical calculations was expected to generate more information to the pyrolysis mechanism of the coal-related model compounds.

2. Experimental

2.1. Materials

BB and BOB as coal-related model compounds were purchased from J&K Chemical Ltd. and TCI, respectively. Absolute ethyl alcohol (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Pyrolysis procedure

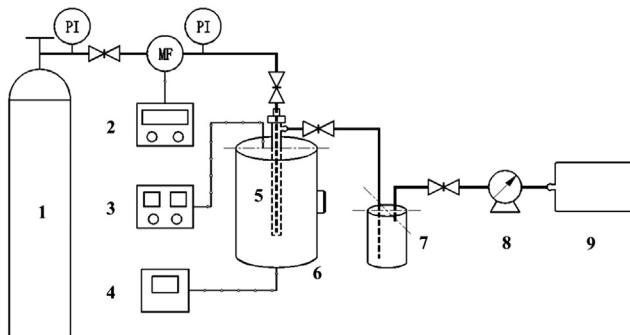
The pyrolysis experiments of model compounds were carried out on a fixed-bed reactor (shown in **Scheme 1**). Firstly, the desired amount of samples was placed in a stainless steel tube reactor (15 mm i.d., 220 mm length), and high-purity nitrogen was flushed to evacuate the air in the system before the pyrolysis experiment. Then the reactor was placed into the preheated furnace (500, 550, 600, 650 and 700 °C), and maintained at the desired temperature for 10 min. After that, the pyrolysis products were brought out by high-purity nitrogen to a cool trap to collect the liquids, whereas the gaseous products were collected by a gas bag. The liquid products were analyzed by gas chromatography–mass spectrometer (GC–MS) and gas chromatography (GC), while the gas products were analyzed by GC. In addition, the weight of the residual char was quantified by weighting the stainless steel tube before and after the pyrolysis. After collecting the products, the tube was heated at 750 °C in air atmosphere for 1 h to remove the residual char. Each experiment was repeated at least five times under the same conditions.

2.3. Analytical methods

Gas chromatograph (TECHCOMP GC 7890II) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used to quantify the gaseous products. The qualitative analysis of liquid product was carried out by GC–MS (HP6890/MS5973) with a HP-5 capillary column (0.25 mm × 30.0 m × 0.25 μm). The quantitative analysis of liquid product was carried out by GC (Agilent 6890N) with a HP-5 capillary column (0.25 mm × 30.0 m × 0.25 μm).

The conversion, yield of gas, liquid and char were calculated using the following equations:

$$\text{Conversion} = \frac{m_0 - m_e}{m_0}, \quad (1)$$



Scheme 1. Flow sheet of experimental apparatus. 1—Nitrogen cylinder, 2—mass flow meter, 3—temperature controller, 4—thermograph, 5—stainless steel tube reactor, 6—furnace, 7—cold trap, 8—wet type gas flow meter, 9—gas bag.

$$\text{Yield of gas, } Y_{\text{gas}} = \frac{m_{\text{gas}}}{m_0}, \quad (2)$$

$$\text{Yield of liquid, } Y_{\text{liquid}} = \frac{m_{\text{liquid}}}{m_0}, \quad (3)$$

$$\text{Yield of char, } Y_{\text{char}} = \frac{m_{\text{char}}}{m_0}, \quad (4)$$

where m_0 is the initial weight of BB or BOB sample before the pyrolysis, m_e is the existing weight of BB or BOB after pyrolysis, m_{gas} is total weight of the gas, m_{liquid} is total weight of the liquid including the existing BB or BOB, and m_{char} is total weight of the char.

3. Computational method

In this paper, all calculations were carried out with Gaussian 09 program [27] by using the density functional theory (DFT) method. The structures of all the reactants, intermediates and products involved in the elementary reactions were optimized with B3LYP (Becke's three parameter gradient corrected exchange functional [28] with the gradient corrected correlation functional of Lee et al. [29]) using the 6-31G (d) basis set [30], which can provide accurate geometrical parameters and energies with low computational cost.

4. Results and discussion

4.1. Pyrolysis of BB

4.1.1. Products analysis of BB pyrolysis

About 0.5 g (2.74 mmol) BB was pyrolyzed for 10 min on a fixed-bed reactor at the desired temperature. The results showed that CH₄, H₂, C₂H₄ and C₂H₆ were gas products. And benzene, toluene, ethylbenzene, styrene, diphenylmethane, trans-stilbene, 1,1-diphenylethane and phenanthrene were the principal liquid products, which account for 97.5–99.1 mol% of total liquid products. There were still two kinds of minor liquid products that had not been defined. In addition, some solid products like char, which adhered to the stainless steel tube and could not dissolve in solvent, were also produced during the pyrolysis.

As shown in **Fig. 1**, the conversion of BB increased from about 20 to 59 wt.% with an increase of temperature from 500 to 700 °C. The yield

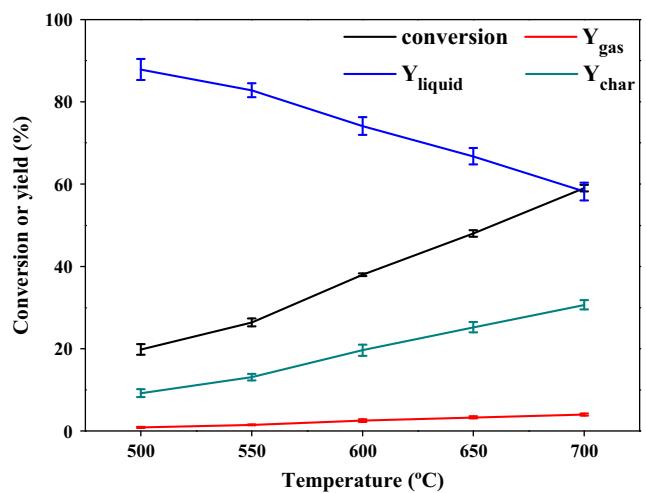


Fig. 1. Conversion, yield of gas, liquid and char at different pyrolysis temperatures for BB (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

of gas and char increased, while that of liquid decreased. This result may be attributed to further reactions among the liquid products, such as carbonization and polymerization, resulting in the decrease of liquid and increase of gas and char yields. That is, these reactions at high temperature are not beneficial for the effective conversion of BB into liquid products. The similar phenomenon also exists in the pyrolysis of coal to oil. The mass balance of BB pyrolysis was about 95.9 ± 2.0 wt.%. The slight mass unbalance may be attributed to the loss in the process of products collection.

As illustrated in Fig. 2, the yields of four gas products increase with raising the temperature, and the increase of CH_4 and H_2 (Fig. 2a) is higher than that of C_2H_4 and C_2H_6 (Fig. 2b). The distribution of liquid products generated from the pyrolysis of BB is shown in Fig. 3. It is found that toluene, styrene, trans-stilbene and phenanthrene are the major products (Fig. 3a), while the yields of benzene, ethylbenzene, diphenylmethane and 1,1-diphenylethane are very low (Fig. 3b). The yields of the above liquid products increase with raising the pyrolysis temperature, but the effect of temperatures on the distribution of products is different. The possible pyrolysis pathways are proposed to explain this phenomenon, and the relationship between the distribution of products and pyrolysis temperature will be discussed in the following section in detail.

4.1.2. Pyrolysis pathways of BB

Based on the experimental results and previous studies, the possible pyrolysis pathways of BB were proposed as Scheme 2. Although many other reactions may occur during the pyrolysis process, the focus of our study is the radical reactions.

There are two initial steps during the pyrolysis of BB: one is the simple homolytic scission of the $\text{C}_{\text{aliphatic}}-\text{C}_{\text{aliphatic}}$ bond (step 1) to produce two resonance stabilized benzyl radicals (P_1), and another is the rupture of $\text{C}_{\text{aryl}}-\text{C}_{\text{aliphatic}}$ bond (step 2) to produce phenyl (P_2) and phenylethyl radicals (P_3). All the pyrolysis products are mainly from further reactions of these three radicals.

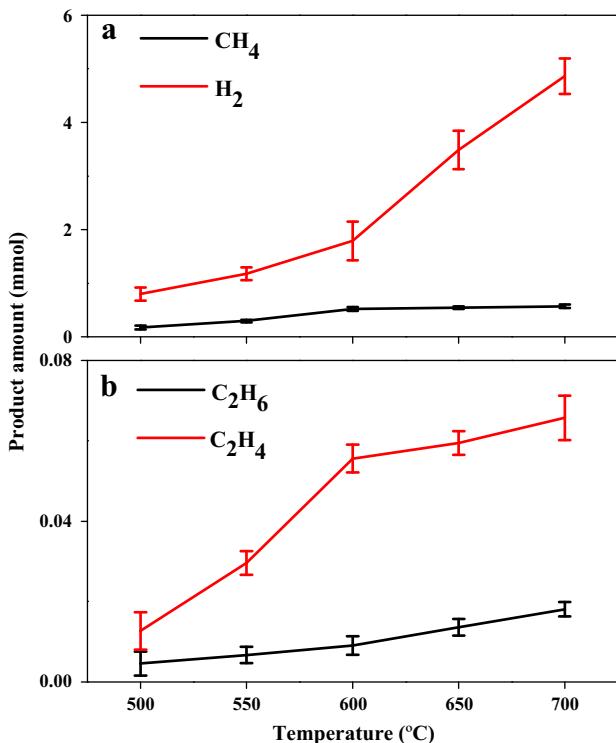


Fig. 2. Distribution of gas products from BB pyrolysis at different temperatures (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

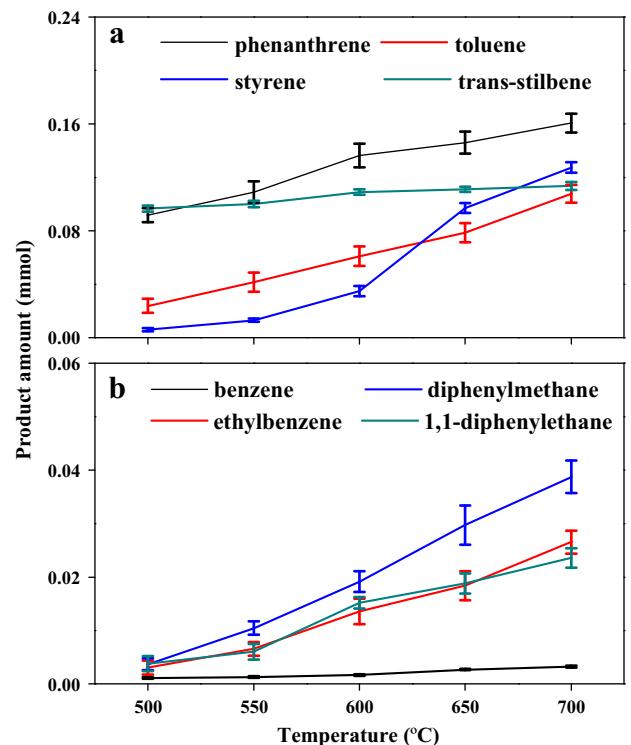


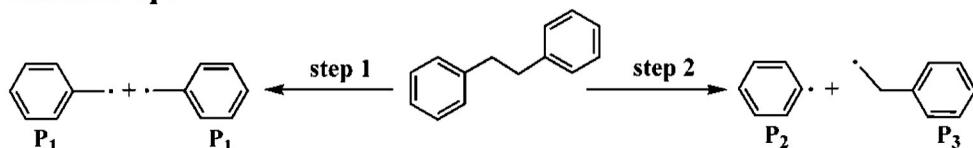
Fig. 3. Distribution of liquid products from BB pyrolysis at different temperatures (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

According to our experimental results, the recombination (step 3) of initial radicals to produce BB and diphenylmethane (P_9) is obviously significant under these experiment conditions. Because there are no hydrogen radical donors to stabilize these initial radicals, the initial produced radicals P_1 , P_2 and P_3 need to be stabilized through hydrogen abstraction from BB (step 4). The hydrogen abstraction would produce benzene, toluene, ethylbenzene and an important intermediate radical P_4 [8,10]. Two major liquid products, trans-stilbene (P_5) and phenanthrene (P_7), are generated from dehydrogenation and cyclization of P_4 [31]. The rearrangement of P_4 is the origination of 1,1-diphenylethane (P_8), and the styrene (P_{10}) is also generated from P_4 through step 9. The four gaseous products are also produced from further reactions and the possible pathways are also shown in Scheme 2.

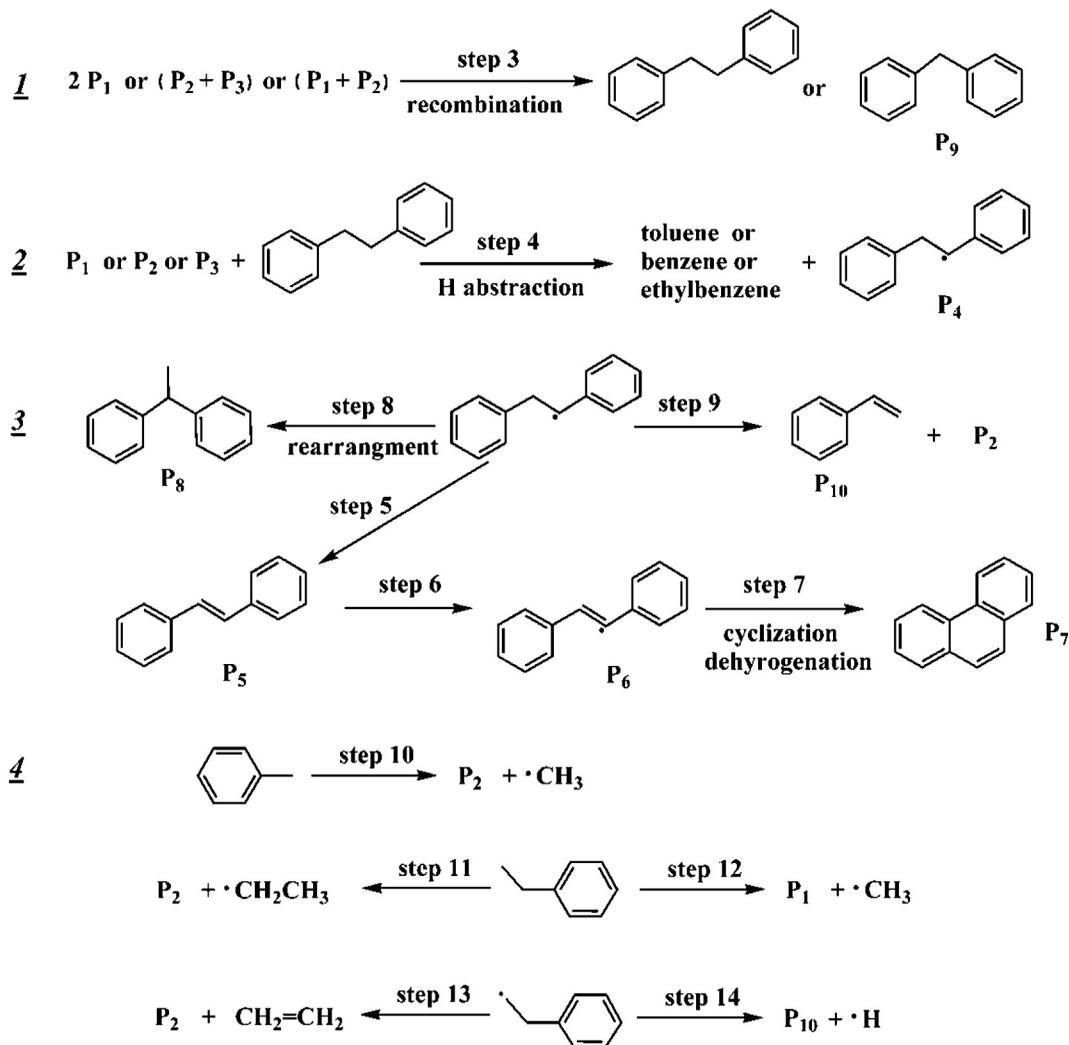
The results in Fig. 3b showed that the yield of benzene, ethylbenzene, and diphenylmethane (P_9) is very low, especially at low temperatures, while toluene is the major product at all temperatures studied, which may be attributed to the easier $\text{C}_{\text{aliphatic}}-\text{C}_{\text{aliphatic}}$ bond homolytic scission than $\text{C}_{\text{aryl}}-\text{C}_{\text{aliphatic}}$ bond rupture. Therefore, it is thought that, for the initial steps, the homolytic scission of the $\text{C}_{\text{aliphatic}}-\text{C}_{\text{aliphatic}}$ bond (step 1) is the primary step during the pyrolysis of BB. The previous study [8] found that toluene is the primary product when no catalyst was used, while trans-stilbene is the primary product when CaO was used as catalyst. However, in this study, the yield of trans-stilbene and phenanthrene is more than that of toluene, suggesting that the direct dehydrogenation of BB to produce trans-stilbene, not through radical reaction, may also exist under these experiment conditions. Additionally, carbonization and polymerization at high temperature in our experiments are other important reactions, which can be evidenced from the decrease of liquid yield and plenty of hydrogen.

To understand the competition of decomposition pathways of BB shown in Scheme 2, the BDEs were calculated by DFT methods at B3LYP/6-31G (d) level.

Initial steps



Further reactions



Scheme 2. The possible pyrolysis pathways of BB.

The BDE of step 1 in Scheme 2 is determined by the following equation:

$$\text{BDE}_{\text{step}1} = E(\text{C}_6\text{H}_5\cdot) + E(\text{C}_6\text{H}_5\cdot) - E(\text{BB}), \quad (5)$$

where E is calculated energy including the zero-point energy correction (ZPE). Energies of optimized reactants and products at different temperatures (500, 600 and 700 °C) were calculated by adding TEMPERATURE key word in frequency calculation route section. Using the same method, the BDEs of the main radical steps in Scheme 2 were calculated, and the results are shown in Table 1.

It is found that all BDEs decrease with raising the temperature, which means that bond rupture becomes easier at high temperature. For the initial steps, the BDE of $\text{C}_{\text{aliphatic}}-\text{C}_{\text{aliphatic}}$ (step 1) is less than that of $\text{C}_{\text{aliphatic}}-\text{C}_{\text{aryl}}$ (step 2), which is also confirmed by the

distribution of liquid products. For the production of CH_4 , step 12 needs less BDE than step 10. Hence, ethylbenzene will be consumed to produce tolyl and methyl radical. Considering the distribution of liquid product and BDE, it can be concluded that the initial step of $\text{C}_{\text{aliphatic}}-\text{C}_{\text{aliphatic}}$ dissociation is the primary step for the pyrolysis of BB.

Table 1
BDEs of the main radical steps in Scheme 2 at different temperatures.

T (°C)	BDE (kJ/mol)				
	Step 1	Step 2	Step 10	Step 11	Step 12
500	235.11	397.13	411.00	395.02	303.60
600	234.14	395.67	409.10	393.54	302.37
700	232.10	393.80	407.91	391.71	301.01

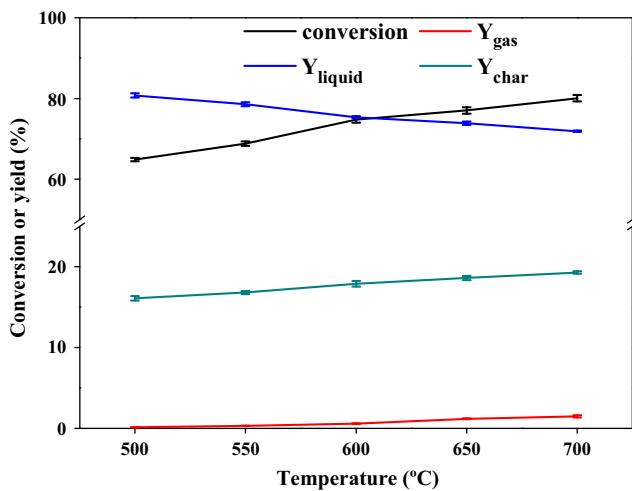


Fig. 4. Conversion, yield of gas, liquid and char at different pyrolysis temperatures for BOB (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

4.2. Pyrolysis of BOB

4.2.1. Products analysis of BOB pyrolysis

The pyrolysis of 1.0 g (5.42 mmol) BOB was carried out at different temperatures, and the gas and liquid products were analyzed. It is found that CH_4 and H_2 were gas products, while benzene, toluene, phenol, styrene, benzyl alcohol, diphenylmethane, trans-stilbene, BB, phenanthrene and o-benzylphenol were the principal liquid products, which account for 97.7–98.7 mol% of total liquid products.

Fig. 4 shows that the pyrolysis temperature has an obvious effect on conversion. When the temperature increased from 500 °C to 700 °C, the conversion rate of BOB increased from about 65 wt.% to 80 wt.%. Also, the varieties of gas, liquid and char yield are similar to those of BB pyrolysis. However, the conversion of BOB is higher than that of BB. The carbonization and polymerization at high temperature to form char and gas also exist during the pyrolysis of BOB. The mass balance during the pyrolysis of BOB was about 94.6 ± 1.7 wt.%.

The production of two gas products increases with raising the pyrolysis temperature from 500 °C to 700 °C (Fig. 5), and the yield of H_2 is higher than that of CH_4 . As shown in Fig. 6, most of the liquid products increase with raising the temperature except BB and o-benzylphenol.

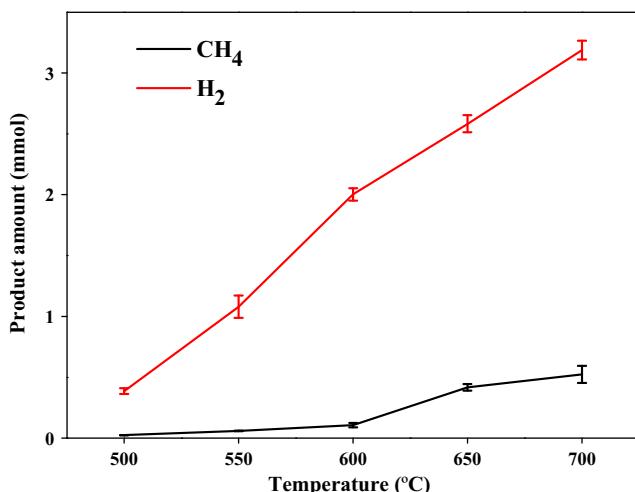


Fig. 5. Distribution of gas products from the BOB pyrolysis at different temperatures (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

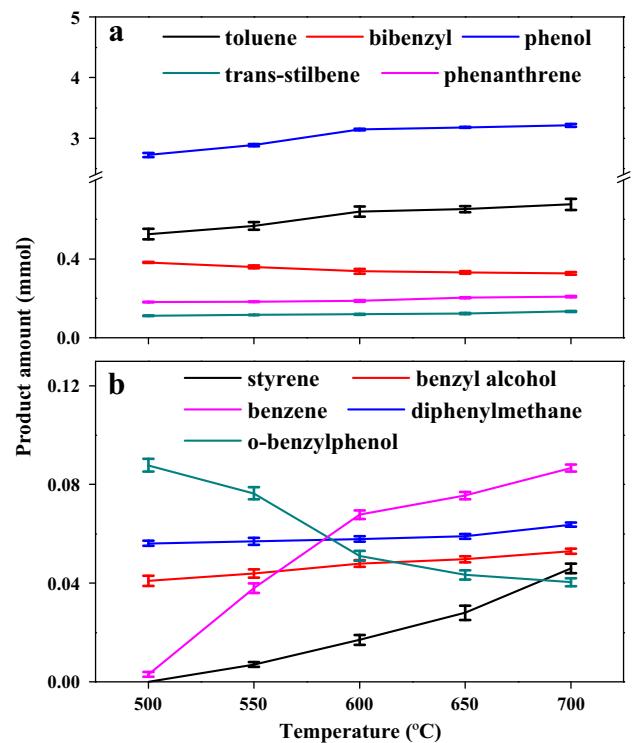


Fig. 6. Distribution of liquid products from BOB pyrolysis at different temperatures (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

4.2.2. Pyrolysis pathways of BOB

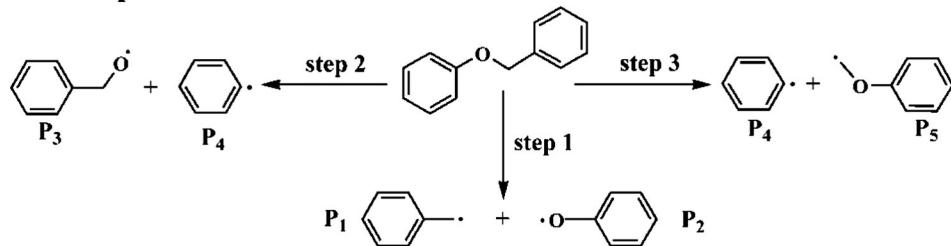
The possible pyrolysis pathways of BOB were proposed as shown in Scheme 3. Because the further reactions of benzyl radicals have been discussed in the BB pyrolysis, these reactions involved in the pyrolysis of BOB will no longer be discussed.

The initial steps of BOB pyrolysis include three kinds of bond dissociation $\text{C}_{\text{aliphatic}}-\text{O}$ (step 1), $\text{C}_{\text{aryl}}-\text{O}$ (step 2), and $(-\text{O}-)\text{C}_{\text{aliphatic}}-\text{C}_{\text{aryl}}$ (step 3) and may produce five radicals (P_1 – P_5). All pyrolysis products are resulted from further reactions of the five radicals.

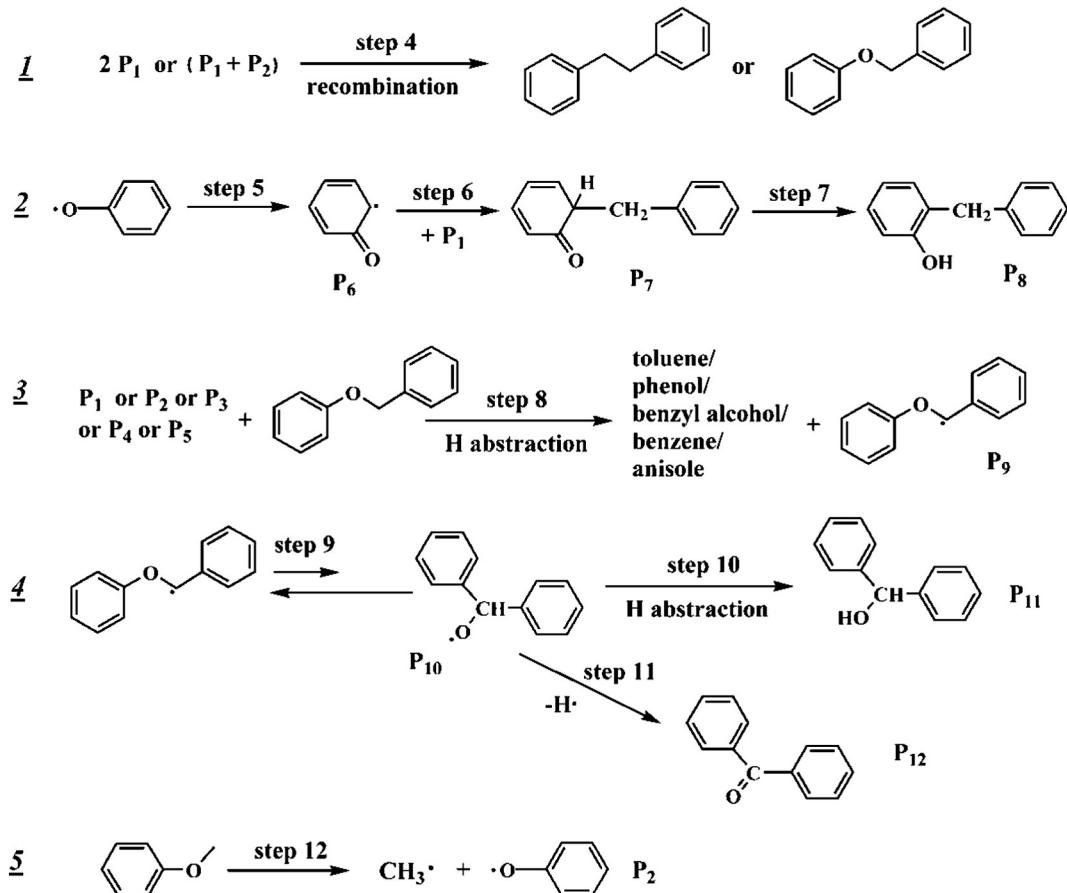
The major product, BB, during the pyrolysis of BOB, is mainly from recombination of two benzyl radicals (P_1). The liquid products styrene, diphenylmethane, trans-stilbene, and phenanthrene are the results of further reactions during the pyrolysis of BB. The phenoxy radical (P_2) will undergo coupling reactions (step 5) to produce the intermediate P_6 [32,33], and the recombination of radical P_6 with benzyl radical (step 6) will produce new intermediate P_7 which can further become o-benzylphenol (P_8) via prototropic rearrangement (step 7) [18]. Additionally, the hydrogen abstraction of initial radicals will generate liquid products benzene, toluene, phenol, benzyl alcohol, anisole, and the intermediate radical P_9 . The radical P_9 undergoes a 1,2-phenyl shift from oxygen to carbon (step 9) followed by either hydrogen abstraction (step 10) to form diphenylmethanol (P_{11}) or hydrogen loss (step 11) to form benzophenone (P_{12}) [18]. However, these two products were not detected in this study.

Regarding to the distribution of liquid products, phenol and toluene are the two primary liquid products, which suggests that the bond dissociation of $\text{C}_{\text{aliphatic}}-\text{O}$ (step 1) be the main pyrolysis pathway during pyrolysis of BOB. The existence of benzyl alcohol indicates that the $\text{C}_{\text{aryl}}-\text{O}$ bond dissociation (step 2) also takes place in this process. The decrease of BB with raising the temperature may be ascribed to the hydrogen abstraction to produce trans-stilbene and phenanthrene at higher temperature. Step 5 and 7 may also be influenced by temperature, which results in the decrease of o-benzylphenol.

Initial steps



Further reactions



Scheme 3. The possible pyrolysis pathways of BOB.

Table 2 lists the BDEs of the main radical reaction steps mentioned in Scheme 3. It can be seen that step 1 has the minimum BDE among the initial steps, which further confirms that the bond dissociation of $\text{C}_{\text{aliphatic}}-\text{O}$ is the primary during the pyrolysis of BOB. The BDE and product distribution also show that $\text{C}_{\text{aryl}}-\text{O}$ bond dissociation (step 2) is a little easier than $(-\text{O}-)\text{C}_{\text{aliphatic}}-\text{C}_{\text{aryl}}$ (step 3).

4.3. Comparison of pyrolysis mechanism of BB and BOB

Although the only difference in structure between BB and BOB is that one carbon atom in the bridge linkage is substituted by one oxygen atom, their pyrolysis behaviors are quite different. From the viewpoint of bond cleavage, there are five kinds of typical bond rupture during the pyrolysis of two model compounds: $\text{C}_{\text{aliphatic}}-\text{C}_{\text{aliphatic}}$ and $(-\text{C}-)\text{C}_{\text{aliphatic}}-\text{C}_{\text{aryl}}$ in BB, $\text{C}_{\text{aliphatic}}-\text{O}$, $\text{C}_{\text{aryl}}-\text{O}$ and $(-\text{O}-)\text{C}_{\text{aliphatic}}-\text{C}_{\text{aryl}}$ in BOB. Their dissociation energies at different temperatures were calculated and listed in Table 3.

It can be seen that the BDEs of five typical bonds are in ascending order of $\text{C}_{\text{aliphatic}}-\text{O} < \text{C}_{\text{aliphatic}}-\text{C}_{\text{aliphatic}} < \text{C}_{\text{aryl}}-\text{O} < (-\text{O}-)\text{C}_{\text{aliphatic}}-\text{C}_{\text{aryl}} < (-\text{C}-)\text{C}_{\text{aliphatic}}-\text{C}_{\text{aryl}}$. This result shows that the existence of O atom can result in the BDE reduction. Therefore, the conversions in pyrolysis of BOB are higher than those in pyrolysis of BB. This is an important information for understanding the conversion of low rank coal with relatively higher oxygen content.

Table 2
BDEs of the main radical steps in Scheme 3 at different temperatures.

T (°C)	BDE (kJ/mol)			
	Step 1	Step 2	Step 3	Step 12
500	186.06	382.64	383.86	242.10
600	186.00	381.67	383.57	241.48
700	185.93	380.68	383.24	240.83

Table 3
BDEs of five typical bonds at different temperatures.

T (°C)	BDE (kJ/mol)				
	C _{aliph} –O	C _{aliph} –C _{aliph}	C _{aryl} –O	(–O–)C _{aliph} –C _{aryl}	(–C–)C _{aliph} –C _{aryl}
500	186.06	235.11	382.64	383.86	397.13
600	186.00	234.14	381.67	383.57	395.67
700	185.93	232.10	380.68	383.24	393.80

In addition, the timely stabilization of the initial radicals is very important for high liquid yield.

5. Conclusion

The pyrolysis mechanisms of two coal-related model compounds, BB and BOB, were studied on a fixed-bed reactor using a stainless steel tube. The pyrolysis experimental results and theoretical calculations indicate that C_{aliphatic}–C_{aliphatic} bond dissociation is the primary step for BB pyrolysis, while C_{aliphatic}–O bond dissociation is the primary step for BOB. The products are mainly generated from further reactions of the initial radicals. The bond cleavage sequence of five typical bonds is in descending order of C_{aliphatic}–O > C_{aliphatic}–C_{aliphatic} > C_{aryl}–O > (–O–)C_{aliphatic}–C_{aryl} > (–C–)C_{aliphatic}–C_{aryl}, which means that the existence of oxygen atom will be beneficial for decreasing the BDE. Although higher conversion can be obtained at high pyrolysis temperature, fewer liquid were produced owing to the carbonization and polymerization. This deduces that it will be important to stabilize the initial radicals by some small radicals timely for improving liquid yield.

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